



Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: Evaluation of different magnesium sources



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HIGHLIGHTS

- Different magnesium sources were evaluated to reduce ammonia inhibition.
- A magnesium based stabilizing agent was used to facilitate struvite precipitation.
- The stabilizing agent was the unique non-harmful magnesium source.
- Anaerobic digestion and struvite precipitation were coupled in the same reactor.

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ABSTRACT

The feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor was evaluated to enhance manure anaerobic digestion methane yields through ammonia inhibition mitigation. Five different magnesium sources were tested as a struvite (ammonia sequestration agent) precursor, i.e. $MgCl_2$, $Mg(OH)_2$, two industrial by-products rich in MgO but with different reactivity, and a stabilizing agent. The latter was formulated in advance with the low reactivity industrial by-product and phosphoric acid. The effect of each magnesium source on anaerobic digestion as well as its struvite precipitation capacity was evaluated through biomethane potential tests. Results indicated that all magnesium sources were able to reduce ammonia concentration to different extents. However, the stabilizing agent was the unique magnesium source that did not inhibit the anaerobic digestion process. The avoidance of adding a phosphate source directly into the digester medium and the high newberyite content were the advantages of the stabilizing agent over the other magnesium sources. Finally, a series of experiments indicated that if anaerobic digestion and struvite precipitation are combined in a single reactor, stabilizing agent addition should be carried out through several small additions rather than few large additions.

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1. Introduction

The capacity to mineralise organic matter, reduce greenhouse gases emissions, produce an effluent with good fertilising qualities and, overall, energy recovery through methane production have made anaerobic digestion (AD) a widely used technology to treat animal manure [1,2]. However, a wide variety of factors have been reported as inhibitors of the AD process and, therefore, to reduce its methane yield [3]. Among all inhibitors, ammonia nitrogen is especially distinct when digesting animal manure [4,5]. Ammonia

nitrogen is produced by the biological degradation of nitrogenous organic matter in the acidogenesis step and it remains in the digester medium in two forms, NH_4^+ and NH_3 , which are in equilibrium depending mainly on temperature and pH [6,7]. Although both forms have been reported as inhibitors of methanogenic activity, the capacity to diffuse into the cell, causing proton imbalance and/or potassium deficiency makes NH_3 the most harmful form [8–10].

Many research efforts have been made to mitigate ammonia nitrogen inhibition in AD. Among them, the addition of material with ion exchange capacity (e.g. bentonite, glauconite, phosphorite and zeolites) or inorganic absorbent materials (e.g. clay, manganese oxides and zeolites) have shown good results [9,11–15]. Likewise, struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation prior or after AD has taken great interest since it is very valuable as slow-releasing

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fertiliser [16]. Struvite precipitation naturally occurs when the combined concentration of Mg^{2+} , NH_4^+ and PO_4^{3-} exceed the struvite solubility product [17,18]. Therefore, the precipitation of struvite in manures requires the addition of chemical compounds since the concentration of Mg^{2+} and PO_4^{3-} are very low in relation to NH_4^+ concentration [19]. Several magnesium ($MgSO_4$, $Mg(OH)_2$, $MgCl_2$, MgO) and phosphate (H_3PO_4 , phosphates salts) sources have been successfully applied to facilitate struvite precipitation [20–22]; nonetheless, the high cost of the pure or high-grade magnesium compounds has limited its full-scale implementation [23]. In this vein, the use of industrial magnesium by-products seems to be a cost-effective alternative to overcome this problem [2,24,25]. Another option to minimise struvite precipitation cost is to combine struvite precipitation and AD in the same reactor; however, this approach has been had limited study. Uludag-Demirer et al. [26] who investigated the effect of $MgCl_2$, $Mg(OH)_2$ and Na_2HPO_4 in batch manure digesters, did not observe any improvement on the methane yield. The authors concluded that the digesters supplied with $Mg(OH)_2$ and Na_2HPO_4 suffered cation (Na^+ and Mg^{2+}) and pH inhibition, while the digesters supplied with $MgCl_2$ and Na_2HPO_4 had only cation inhibition. Contrariwise, Lee et al. [27] satisfactorily operated a continuous biowaste digester combined with struvite precipitation, where $MgCl_2$ was added to reach a Mg:P molar ratio of 1:1 and pH was adjusted between 7.7 and 8.3. The authors concluded that the 50% methane production improvement was due to the reduction of ammonia nitrogen concentration from 6.0 to 2.0 g N L⁻¹. Similarly, Romero-Güiza et al. [2] recorded a 25% and 40% methane production improvement when dosing 5 and 30 g L⁻¹ of a stabilizing agent formulated with low-grade magnesium oxide, respectively, in a continuous pig manure digester. The authors related the methane yield improvement to the reduction of the ammonia concentrations, the increase of magnesium concentration, and the presence of particles in the digester medium. Even though the literature is scarce, the disparity between studies suggest that there are aspects from the magnesium sources that have not been considered (e.g. cation availability, reagent solubility and reactivity) but which might have a significant role on the feasibility of this promising approach.

The main goal of this study was to compare the performance of five different magnesium sources (i.e. $MgCl_2$, $Mg(OH)_2$, high-grade MgO, low-grade MgO and a stabilizing agent) in reactors coupling anaerobic digestion and struvite precipitation. The study also aims to identify the factors that may limit the applicability of combining both processes in a single reactor.

2. Materials and methods

2.1. Analytical methods

The major and minor components of the magnesium sources and the loss of ignition (LOI) were determined by X-ray fluorescence (XRF) using a Philips PW2400 X-ray sequential spectrophotometer. X-ray diffraction patterns were performed in a Bragg-Brentano Siemens D-500 powder diffractometer with $CuK\alpha$ radiation to obtain information about the crystalline phases. Scanning electronic micrographs were obtained with a SEM Quanta 200 FEI analyser equipped with an energy dispersive spectrometer analyser. The reactivity of the MgO samples was determined by the citric acid method, which measures the time needed by 2.0 g of powdered MgO in 100 mL of 0.4 N citric acid solution to reach pH 8.2. Citric acid results indicate the hydration and dissolution capability of the MgO particles [28]. The specific surface area of the MgO samples was determined using the BET single point method with a Micromeritics Tristar 3000 porosimeter.

Total solids (TS) and volatile solids (VS) were determined following the guidelines given by the standard methods 2540G [29]

with minor modifications [30]. Inorganic carbon (IC) were measured by means of a Shimadzu 5055 TOC-VCSN TOC analyser. Individual volatile fatty acids (VFAs; acetate, propionate, butyrate and valerate) were analysed by a HP 5890-Serie II chromatograph as for Astals et al. [31]. Anions (Cl^- and PO_4^{3-}) and cations (NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) were determined in an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns [32]. Total ammonia nitrogen (TAN) comprises both forms NH_4^+ and NH_3 , while total phosphate (TP) is the sum of $H_2PO_4^-$ and HPO_4^{2-} (main phosphate species under assay pH conditions). Biogas composition was analysed by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column (Carboxen[®] – 1010 PLOT) and a thermal conductivity detector [2].

2.2. Pig manure, inoculum and chemical reagents origin

Pig manure and digested pig manure, used as inoculum, were collected from a centralized mesophilic anaerobic digestion plant, which treats around 100,000 tons of pig manure per year. After collection, both samples were stored at 4 °C. Prior to commencement of the biomethane potential (BMP) tests inoculum was degassed at 37 °C for one week. Pig manure and the inoculum characterisation is given in Table 1.

Analytical grade $MgCl_2$, $Mg(OH)_2$, and K_2HPO_4 were purchased from Panreac Quimica, S.A. (Barcelona, Spain). The two industrial by-products, named as high-grade magnesium oxide (HG-MgO) and low-grade magnesium oxide (LG-MgO) according to their MgO content, were provided by Magnesitas Navarras, S.A. (Navarra, Spain). HG-MgO and LG-MgO were obtained from the calcination of natural magnesite in rotary kiln at 1100 °C to obtain caustic calcined magnesia. HG-MgO is the finest fraction (<1 mm) of the calcined magnesia collected at the bottom of the furnace, while LG-MgO is a by-product collected as cyclone dust in the fabric filters from the air pollution control system. The stabilizing agent (SA) was formulated with LG-MgO and phosphoric acid following Romero-Güiza et al. [2]. Briefly, phosphoric acid was slowly added to an aqueous slurry of LG-MgO with a high solid-to-liquid ratio. The exothermic acid–base reaction generated a solid with a high content of newberyite ($MgHPO_4 \cdot 3H_2O$) and other magnesium phosphate compounds, which inner core did not react on the basis of the shrinking core model and remained as LG-MgO. Then, the

Table 1
Pig manure and inoculum characterization.

	Units	Pig manure	Inoculum
TS	g L ⁻¹	32.1	47.2
VS	g L ⁻¹	21.0	29.9
pH	–	7.5	8.0
TAN	mg N L ⁻¹	1785	2490
TP	mg P L ⁻¹	36	33
Mg^{2+}	mg L ⁻¹	37	36

Table 2
Semi-quantitative characterisation of HG-MgO, LG-MgO and SA.

	Units	HG-MgO	LG-MgO	SA
MgO	%	89.8	63.4	31.8
P ₂ O ₅	%	–	–	32.8
CaO	%	1.5	8.7	4.7
SO ₃	%	–	3.8	1.1
Fe ₂ O ₃	%	–	2.4	1.2
SiO ₂	%	–	3.2	0.9
V ₂ O ₅	%	–	0.3	0.3
MnO	%	–	0.1	0.1
LOI (1100 °C)	%	3.3	8.9	24.7
Reactivity	s	90	2280	>3000
BET surface area	m ² g ⁻¹	8.83	10.87	11.94

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